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(54) Sulfur-free lubricating composition

(57) A sulfur-free lubricating composition comprises a major portion of a polyalphaolefin(s) base lubricating oil and defined minor portions of a tri(alkylphenyl)

(phosphate or di(alkylphenyl)phosphoric acid antiwear agent, an amine antioxidant, a substituted succinamide rust inhibitor, and a polytriazole.

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Description

[0001] This invention relates to sulfur-free lubricating oil compositions.

BACKGROUND OF THE INVENTION

[0002] Synthetic lubricants find increasing utility because of their uniformity and because they are free of undesirable sulfur constituents. In order to meet users increasingly stringent criteria, these synthetic lubricating oils are typically modified by the addition of additives such as ashless antiwear agents, corrosion inhibitors, antioxidants and the like.

[0003] Although phosphorous-containing anti-wear additives have been proposed for use in synthetic lubricating oils, their use is associated with certain drawbacks. In general phosphorous-containing anti-wear additives are poor extreme pressure agents. Moreover, their thermal and oxidation stability are poor, giving rise to metal corrosive species and sludge. Similarly, sulfur and phosphorous containing antiwear additives have been proposed for use in synthetic lubricating oils and while these additions tend to have good extreme pressure properties, they too are not very thermally stable and give rise to corrosive decomposition products.

[0004] Polyol esters have been used in synthetic lubricants as an additive and sludge solubilizing medium; however, it appears that increased amounts of polyol esters also decompose to form corrosive species.

[0005] Thus, there remains a need for synthetic lubricant compositions with good antiwear and extreme pressure properties and enhanced thermal/oxidation stability.

SUMMARY OF THE INVENTION

[0006] According to the invention, there is provided a sulfur free lubricating composition comprising a major portion of a synthetic base lubricating oil and a minor portion of a tri(alkyl phenyl)phosphate or di(alkylphenyl)phosphoric acid antiwear agent, an amine antioxidant a substituted succinamide rust inhibitor and a tolytriazole.

[0007] The tri(alkylphenyl)phosphate or di(alkylphenyl)phosphoric acid antiwear agent is incorporated in the oil in an amount ranging between about 0.1 to 2.0 wt% and the amine antioxidant in amount ranging from about 0.1 to 5 wt%. The succinamide is present in an amount ranging from about 0.01 to 0.5 wt% and the tolytriazole, from about 0.01 to 0.5 wt%. In the foregoing, the wt% is based on the weight of oil.

[0008] This and other embodiments will be described in detail hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

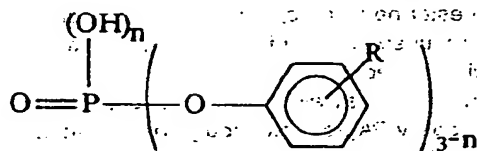
[0009] The synthetic base lubricating oil useful in the present invention is any polyalphaolefin (PAO) or mixtures thereof having a kinematic viscosity of about 1.8 to about 300 cSt at 100°C. These oils are inherently free of sulfur, phosphorous and metals.

[0010] Polyalphaolefins are prepared by the oligomerization of 1-decene or other olefins to produce lubricant range hydrocarbons.

[0011] The synthetic base oil, of course, comprises the major portion of the lubricating composition of the invention. Typically, the base oil will comprise from about 50 to about 95 wt% of the total composition.

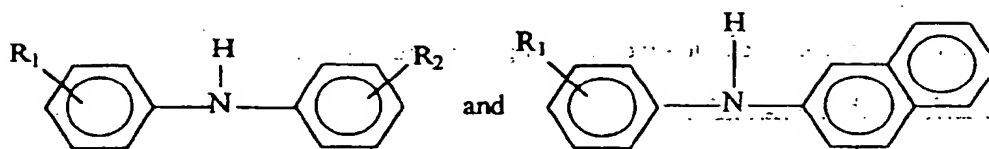
[0012] Incorporated in the composition is a minor portion of a tri(alkylphenyl)phosphate antiwear (AW) agent, an amine antioxidant (AO), a succinamide rust inhibitor (RI) and a tolytriazole.

[0013] The tri(alkylphenyl)phosphate or di(alkylphenyl)phosphoric acid useful in the composition of this can be represented by the formula:



where n is 0 or 1 and wherein R is an alkyl group of from about 2 to about 6 carbon atoms, and preferably 3 to 4 carbon atoms. In general, the tri(alkylphenyl)phosphate or di(alkylphenyl)phosphoric acid is present in an amount ranging between about 0.1 to about 2.0 wt% based on the weight of the oil and preferably from about 0.7 to about 1.0 wt%.

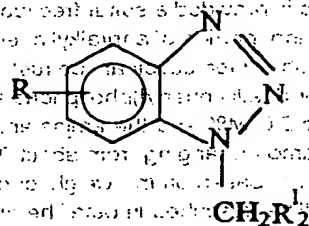
[0014] Although any amine antioxidant used in lubricant compositions may be employed, it is particularly preferred to use phenyl amines; phenyl naphthylamines and their alkylated derivatives which can be represented by the formula:



wherein R_1 and R_2 are independently H and alkyl groups having from about 3 to about 14 carbon atoms and preferably 4 to 9 carbon atoms. In general, the amine antioxidant will be present in an amount ranging from about 0.1 to 5 wt% based on the weight of oil and preferably, about 0.5 to 1.5 wt%.

[0015] Included in the composition of the present invention is a substituted succinamide rust inhibitor. Such succinamide compounds are well-known in the art. In the present invention, preferred succinamide compounds are those formed by reacting an amino acid amide with an alkenyl succinic acid or succinic anhydride. Illustrative of amino acid amides are those compounds formed by reacting a polyamine such as triethylene tetramine with a monocarboxylic acid such as oleic acid. Illustrative alkenyl succinic acids are decenyl, dodecenyl, tetradecenyl succinic acid. Typically, the substituted succinamide will be present in an amount ranging from about 0.02 to about 0.3 wt% based on the weight of the oil, and preferably about 0.04 to 0.15 wt%.

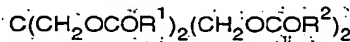
[0016] The tolyltriazoles suitable as a minor portion of the compositions of the invention are hydrocarbon substituted tolyl 1,2,3 triazoles, amino alkyl substituted 1,2,3 tolyl triazoles and alkyl amino alkyl 1,2,3 tolyl triazoles. A particularly preferred tolyl triazole is represented by the formula:



wherein R and R^1 are independently hydrogen or a C_1 to C_{20} hydrocarbyl radical.

[0017] Typically, the tolyltriazole will be present in an amount ranging from about 0.01 to about 0.5 wt% based on the weight of oil and preferably 0.03 to 0.2 wt%.

[0018] The compositions of the invention may also include an polyol ester solubilizer. Suitable esters may comprise diesters of aliphatic C_6 to C_{12} dicarboxylic acids, and those made from C_5 to C_{12} monocarboxylic acids and polyols. Diesters, triesters, tetra-esters and mixtures thereof are useful in the present invention typically have molecular weight ranging from about 350 to about 1000. Particularly preferred is a neopentyl polyol ester represented by the formula:



wherein R^1 is a linear of 7 to 9 carbon alkyl group and R^2 is a branched alkyl group of from 5 to 10 carbon atoms, and preferably 7 carbon atoms.

[0019] In general, the ester solubilizer will not exceed more than about 30 wt% of the total weight of the composition. Indeed, it is preferred that a polyol ester be incorporated in the composition only when the viscosity of the synthetic base oil is such that a solubilizer is required for the additives. Typically, when the viscosity of the oil is above about 12 cSt at 100°C an ester solubilizer will be used.

[0020] The compositions of the invention may also include a thickener to increase the viscosity of the composition. Suitable thickness includes high viscosity PAO's, polyisobutylene, ethylene propylene copolymers and similar thickeners. In general, these thickeners will not exceed 30 wt% based on the weight of oil.

[0021] The following examples will serve to further illustrate the invention.

EXAMPLES

[0022] The following nineteen lubricating oil compositions demonstrate formulations of the present invention. The composition of each formulation is given in the Table of Formulations. Identification of the components used in the

formulation is given in the Table of Components. These lubricating oil compositions were subjected to various tests which along with the test results are listed in the Table of Tests and Results.

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TABLE OF FORMULATIONS

COMPONENTS	F O R M U L A T I O N S									
	1	2	3	4	5	6	7	8	9	10
Base Oil, wt%										
A	39.1									
B	43.93	76.1								
C		16.93	91.3	74.4	64.32	45.4	28.4	11.03		
D			1.73	18.63	23.71	42.63	59.63	77	76.8	45.2
E	10								11.2	42.8
AW Additive, wt%										
F	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Amines, wt%										
G	1	1	1	1	1	1	1	1	1	1
H										
Rust Inhibitor, wt%										
I	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Tolyltriazole, wt%										
J	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ester, wt%										
K	5	5	5	5	5	5	5	5	5	5
L										
M										
N										
Thickener, wt%										
O					5	5	5	5	5	5

TABLE OF FORMULATIONS (continued)

COMPONENTS	F O R M U L A T I O N S															
	11	12	13	14	15	16	17	18	19							
Base Oil, wt%																
A																
B																
C			77.03	77.03	77.03	77.03	77.03	77.03								
D	14		16	16	16	16	16	16	59.03							
E	74	77							24							
AW Additive, wt%																
F	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8							
Amines, wt%																
G	1	1	1	1	1	1	1	1	1							
H																
Rust Inhibitor, wt%																
I	0.1	0.1	0.07	0.07	0.07	0.07	0.07	0.07	0.07							
Tolyltriazole, wt%																
J	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1							
Ester, wt%																
K	5	5	5					5	5							
L				5			5									
M					5											
N						5										
Thickener, wt%																
O	5	16							10							

TABLE OF COMPONENTS

BASE OILS	A	PAO-2	Polyalphaolefins; 2 cSt @ 100°C; Oronite
	B	PAO-6	Polyalphaolefins; 6 cSt @ 100°C; Ethyl or Mobil
	C	PAO-8	Polyalphaolefins; 8 cSt @ 100°C; Ethyl or Mobil
	D	PAO-40	Polyalphaolefins; 40 cSt @ 100°C; Mobil
	E	PAO-100	Polyalphaolefins; 100 cSt @ 100°C; Mobil
AW AGENT	F	Durad 310M	Tri-(isopropylphenyl)phosphate; FMC
AMINE	G	Naugalube 438L	Di-nonyl-diphenylamine; Uniroyal
RUST INHIBITOR	I	Hiitec 536	Alkenyl succinamide derivative; Ethyl Corp.
TOYL-TRIAZOL	J	Irgamet 39	1,2,3 tolyltriazole derivative
ESTERS	K	NP-439	Reaction product of Pentaerythritol and aliphatic and branched carboxylic acids; Exxon Chemical Co.
	L	NP-353	Reaction product of Trimethylol propane and aliphatic and branched carboxylic acids; Exxon Chemical Co.
	M	DOS	Di-octylsebacate
	N	NP-317	Reaction product of Trimethylol propane and aliphatic and branched carboxylic acids
THICKENER	O	Parapoid 11279	Polyisobutylene with averaged MW of about 2500; Exxon Chemical Co.

TABLE OF TEST AND RESULTS

Test	Test Method	F O R M U L A T I O N S									
		1	2	3	4	5	6	7	8	9	10
Viscosity at 40°C	D445	19.81	32.6	47	66.9	98	147	214.1	317.5	467.1	678.3
Viscosity at 100°C	D445	4.58	6.08	7.82	10.24	13.66	18.5	24.41	32.61	43.81	60.1
Rust Test	D665B	P	P								P
Rust Test	D665B	P	P					P			P
Cu Corrosion at 121°C	D130		1A					1B			1B
4 Ball Wear (mm WSD)	D2266		0.36								
Demulsibility	D1401		41-39-0					41-39-0			43-37-0
Demulsibility; % water in oil	D2711		0.1					0.8			1.4
Demulsibility; Emulsion	D2711		0					0			0
Demulsibility; free water (ml)	D2711		86					84.9			80.1
Foaming: Seq I	D892		0/0				0/0				0/0
Foaming: Seq II	D892		0/0				0/0				30/0
Foaming: Seq III	D892		0/0					0/0			0/0
Rotary Bomb	D2272		1105	1155; 1400						1300	
Oxidation test (min)											
Oxidation test (% Vis Increase)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sludge Test (mg/100 ml)	D4310		25								
Cincinnati-Milacron Thermal	A										
Test: Sludge (mg/100 ml)			3.8								
Wear test (FLS)	FZG		>12		>13			>12			>13

TABLE OF TEST AND RESULTS (continued)

Test	F O R M U L A T I O N S									
	Test Method	11	12	13	14	15	16	17	18	19
Viscosity at 40°C	D445	969.8	1455.5							
Viscosity at 100°C	D445	80.3	107.8							
Rust Test	D665B	P	P							
Rust Test	D665B			P						P
Cu Corrosion at 121°C	D130		IB	IB						IB
4-Ball Wear (mm WSD)	D2266			0.325						
Demulsibility	D1401		43-37-0	42-38-0						42-38-0
Demulsibility, % water in oil	D2711									
Demulsibility, Emulsion	D2711									
Demulsibility, free water (ml)	D2711		86					84.9		
Foaming: Seq I	D892		0/0	0/0						
Foaming: Seq II	D892		0/0	20/0						
Foaming: Seq III	D892		0/0	0/0						
Rotary Bomb Oxidation (min)	D2272			1605	1800	1993	1635	1905	1530	1600
Oxidation test (% Vis Increase)	D2893									
Sludge Test (mg/100 ml)	D4310			25.5	72	20.7	30.5	10.2		6.3
Cincinnati-Milacron Thermal	A									
Test: Sludge (mg/100 ml)				4	4.4		3.6	13.55	6.4	11.1
Wear test (FLS)	FZG									>13

Claims

1. A sulfur-free lubricating composition comprising:
a major portion of at least one polyalphaolefin base lubricating oil; and, based on the weight of oil,

1. The first part of the report is a general introduction to the project. It describes the purpose of the study, the scope of the work, and the organization of the report.

2. The second part of the report is a detailed description of the methodology used in the study. It includes a discussion of the data sources, the data collection methods, and the data analysis techniques.

<p>3. The third part of the report is a detailed description of the results of the study. It includes a discussion of the findings, the conclusions, and the implications of the study.</p>	<p>4. The fourth part of the report is a detailed description of the conclusions and implications of the study. It includes a discussion of the findings, the conclusions, and the implications of the study.</p>
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5. The fifth part of the report is a detailed description of the conclusions and implications of the study. It includes a discussion of the findings, the conclusions, and the implications of the study.

(19)



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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 2071

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 97 16827 A (BORELIS LOUIS ; KHAN RAQUIB U (US); LEUTHOLD HANS (US); HEINE GUNTE) 9 May 1997 (1997-05-09) * page 4, line 22 - page 5, line 5 * * page 10, line 26 - page 10, line 30 * * page 12, line 30 - page 13, line 4 * * page 13, line 31 - page 15, line 12 *	1-9	C10M169/04 //(C10M169/04, 107:02,129:72, 129:74,133:12, 133:16,133:56, 133:44, 137:04), (C10M169/04, 107:02,129:74, 133:12,133:44, 137:04)
X	US 5 133 888 A (WAYNICK JOHN A) 28 July 1992 (1992-07-28) * page A * * column 2, line 9 - column 6, line 21 * * example 14 *	1-9	
A	WO 95 29214 A (MARKSON ANDREW JONATHAN (GB); PRAGNELL JOHN WILLIAM A) 2 November 1995 (1995-11-02) * the whole document *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10M
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 23 February 2000	Examiner Perakis, N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 2071

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23-02-2000

Patent document cited in search report	Publication date	Patent family members)	Publication date
WO 9716827 A	09-05-1997	CN 1200833 A	02-12-1998
		CN 1200834 A	02-12-1998
		DE 19681633 T	29-10-1998
		DE 19681634 T	03-12-1998
		GB 2322728 A,B	02-09-1998
		GB 2322729 A	02-09-1998
		JP 11514778 T	14-12-1999
		JP 11514779 T	14-12-1999
		WO 9716828 A	09-05-1997
		WO 9716829 A	09-05-1997
		US 5930075 A	27-07-1999
		US 5907456 A	25-05-1999
US 5133888 A	28-07-1992	NONE	
WO 9529214 A	02-11-1995	AU 695511 B	13-08-1998
		AU 2313595 A	16-11-1995
		CN 1151174 A,B	04-06-1997
		EP 0757712 A	12-02-1997
		JP 10503535 T	31-03-1998
		NZ 284520 A	22-09-1997

EPO FORM P0489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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